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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1140). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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[1,1'-Bis(diphenylphosphinato-O)-ferrocene]tetrachlorotin

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Abstract

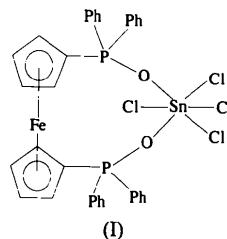
The structure of the title compound, [SnCl₄(C₃₄H₂₈FeO₂P₂)], shows the 1,1'-bis(diphenylphosphino)ferrocene ligand connected to an octahedral Sn atom through the formation of P—O bonds. The molecule has near twofold rotational symmetry through the line joining the Fe and Sn atoms. The cyclopentadienyl (Cp) rings are perfectly eclipsed but the two C_{Cp}—P bonds are at an angle of 72° about the centroids of the Cp rings.

Comment

Complexes of the type (dppf)MCl₂ [dppf = 1,1'-bis(diphenylphosphino)ferrocene; M = Pt, Pd, Ni], where

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dppf acts as a bidentate ligand, have been reported together with their X-ray structures (Clemente, Piloni, Corain, Longato & Camellini, 1986; Casellato, Ajo, Valle, Corain, Longato & Graziani, 1988). Alternatively, (dppf)bis(chlorogold) is an example of a complex where dppf acts either as a monodentate ligand or as a bridge connecting the two Au atoms (Hill *et al.*, 1989). Recently, diphenylphosphinomethane (dppm) and (+)-(R,R)-1,2-bis(methylphenylphosphino)benzene (P*2) have been reported to give monodentate [SnCl₄(dppm)₂] and bidentate [PhSnCl₃(P*2)], respectively, when reacted with phenyltin trichloride (Dakternieks, Zhu & Tiekink, 1994). We have studied the reaction of dppf with SnCl₄ and found that there is oxidation at the P centres resulting in the formation of the title compound, [Fe(5-C₅H₄PPh₂O)₂SnCl₄], (I).



A displacement ellipsoid plot of the title molecule together with the numbering scheme is shown in Fig. 1. The Sn atom has octahedral coordination with the O1 atom *cis* with respect to the O2 atom. Atoms C11 and C12 are *trans* to atoms O2 and O1, respectively. The Sn—C11 and Sn—C12 distances are longer than the other two Sn—Cl distances and this may be attributed to the *trans* effect of oxygen. These variations in Sn—Cl bond length and a C13—Sn—C14 bond angle of 168.38(3)° result in the geometry around the Sn atom deviating slightly from ideal octahedral geometry. The geometry about both P atoms is tetrahedral; the average P—C_{Cp} and P—C_{phenyl} bond lengths of 1.779(3)

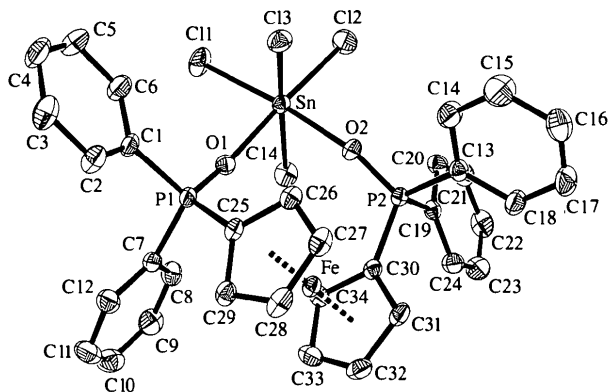


Fig. 1. A 30% probability displacement ellipsoid plot of the title molecule showing the numbering scheme.

and 1.795 (3) Å, respectively, are shorter than the corresponding bond lengths observed in the dppf molecule [1.819 (5) and 1.835 (4) Å; Casellato, Ajo, Valle, Corain, Longato & Graziani, 1988].

The cyclopentadienyl (Cp) rings are planar and the dihedral angle between the planes is 2.13 (1)°. In the dppf molecule, the Cp rings are staggered and the C_{Cp}—P bonds are *trans* with respect to one another. In the present complex, however, the formation of the Sn—O—P link has resulted in the Cp rings being rotated by 108° with respect to one another and their having an eclipsed conformation. The P1—O1—Sn and P2—O2—Sn angles of 161.5 (1) and 158.9 (1)° are sufficiently wide enough to incorporate the dppf molecule in the complex. The dihedral angle between the C1—C6 and C7—C12 phenyl rings is 56.6 (1)° and they, in turn, make angles of 83.8 (1) and 65.1 (1)° with their associated C25—C29 Cp ring. Similarly, the angle between the C13—C18 and C19—C24 phenyl rings, and their angles with the C30—C34 Cp ring are 80.8 (1), 61.9 (1) and 90.5 (1)°, respectively. The molecule has near twofold rotational symmetry with the rotation axis passing through the Fe and Sn atoms. There are two intermolecular C—H...Cl contacts; C5...Cl3ⁱ 3.676 (5) Å and C5—H5...Cl3ⁱ 160 (4)°, which connects centrosymmetrically related molecules, and C15...Cl4ⁱⁱ 3.467 (5) Å and C15—H15...Cl4ⁱⁱ 139 (5)°, which connects glide-related molecules [symmetry codes: (i) 1 - x, -y, -z; (ii) x - 1/2, 1/2 - y, z - 1/2].

Experimental

The title compound was prepared by adding 1,1'-bis(diphenylphosphino)ferrocene to a solution of tin tetrachloride in acetonitrile. The resulting solution was allowed to stand for 3 d whereupon yellow crystals suitable for X-ray analysis were obtained.

Crystal data

[SnCl₄(C₃₄H₂₈FeO₂P₂)]

M_r = 846.84

Monoclinic

*P*2₁/*n*

a = 12.221 (3) Å

b = 20.750 (3) Å

c = 13.902 (2) Å

β = 106.94 (2)°

V = 3372.4 (11) Å³

Z = 4

D_x = 1.668 Mg m⁻³

D_m not measured

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 8–25°

μ = 1.614 mm⁻¹

T = 293 (2) K

Needle

0.60 × 0.22 × 0.14 mm

Yellow

9197 measured reflections

7657 independent reflections

6084 observed reflections

[*I* > 2σ(*I*)]

*R*_{int} = 0.0219

Refinement

Refinement on *F*²

R(*F*) = 0.0331

wR(*F*²) = 0.0912

S = 0.980

7657 reflections

509 parameters

All H-atom parameters

refined

w = 1/[σ²(*F*_o²) + (0.0526*P*)²]

where *P* = (*F*_o² + 2*F*_c²)/3

3 standard reflections

monitored every 97

reflections

intensity decay: <4%

(Δ/σ)_{max} = 0.001

Δρ_{max} = 0.983 e Å⁻³

Δρ_{min} = -0.655 e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *Crystallography* (1992),

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Sn	0.84792 (2)	0.094557 (9)	0.149658 (14)	0.03124 (7)
Fe	0.77014 (3)	0.27348 (2)	0.36381 (3)	0.02872 (10)
C11	0.80788 (10)	-0.01835 (4)	0.14183 (8)	0.0613 (3)
C12	0.93604 (9)	0.09207 (5)	0.01780 (7)	0.0596 (2)
C13	0.66763 (7)	0.12560 (4)	0.03927 (6)	0.0470 (2)
C14	1.02173 (7)	0.08133 (4)	0.27981 (7)	0.0507 (2)
P1	0.68307 (7)	0.11898 (3)	0.32187 (5)	0.0303 (2)
P2	0.93715 (6)	0.25623 (3)	0.21058 (5)	0.02728 (14)
O1	0.7690 (2)	0.10365 (9)	0.2666 (2)	0.0359 (5)
O2	0.8779 (2)	0.19457 (9)	0.1686 (2)	0.0353 (4)
C1	0.5502 (3)	0.07852 (14)	0.2668 (2)	0.0365 (6)
C2	0.4501 (3)	0.0968 (2)	0.2885 (3)	0.0508 (9)
C3	0.3475 (4)	0.0659 (2)	0.2415 (4)	0.0658 (11)
C4	0.3433 (4)	0.0188 (2)	0.1723 (3)	0.0661 (12)
C5	0.4404 (4)	0.0004 (2)	0.1506 (3)	0.0664 (12)
C6	0.5446 (4)	0.0296 (2)	0.1975 (3)	0.0514 (9)
C7	0.7436 (3)	0.09573 (14)	0.4516 (2)	0.0356 (6)
C8	0.8578 (3)	0.0785 (2)	0.4836 (3)	0.0456 (8)
C9	0.9100 (4)	0.0661 (2)	0.5845 (3)	0.0585 (10)
C10	0.8472 (5)	0.0704 (2)	0.6526 (3)	0.0641 (12)
C11	0.7350 (4)	0.0865 (2)	0.6210 (3)	0.0603 (11)
C12	0.6815 (4)	0.0989 (2)	0.5206 (3)	0.0479 (8)
C13	0.8801 (3)	0.31982 (14)	0.1234 (2)	0.0338 (6)
C14	0.7865 (4)	0.3071 (2)	0.0420 (3)	0.0570 (10)
C15	0.7413 (5)	0.3565 (2)	-0.0244 (4)	0.084 (2)
C16	0.7895 (5)	0.4172 (2)	-0.0105 (4)	0.0697 (13)
C17	0.8840 (4)	0.4290 (2)	0.0679 (3)	0.0582 (10)
C18	0.9297 (3)	0.3806 (2)	0.1358 (3)	0.0468 (8)
C19	1.0884 (2)	0.25366 (14)	0.2281 (2)	0.0315 (6)
C20	1.1282 (3)	0.2177 (2)	0.1602 (2)	0.0410 (7)
C21	1.2441 (3)	0.2184 (2)	0.1696 (3)	0.0516 (9)
C22	1.3180 (3)	0.2526 (2)	0.2442 (3)	0.0583 (10)
C23	1.2794 (3)	0.2873 (2)	0.3117 (3)	0.0550 (9)
C24	1.1639 (3)	0.2877 (2)	0.3039 (2)	0.0448 (8)
C25	0.6510 (2)	0.20285 (13)	0.3215 (2)	0.0312 (6)
C26	0.6441 (3)	0.24539 (14)	0.2386 (2)	0.0351 (6)
C27	0.6209 (3)	0.3079 (2)	0.2683 (3)	0.0418 (7)
C28	0.6124 (3)	0.3053 (2)	0.3674 (3)	0.0440 (8)
C29	0.6308 (3)	0.24049 (15)	0.4013 (3)	0.0373 (7)
C30	0.9192 (2)	0.27787 (14)	0.3284 (2)	0.0304 (6)
C31	0.8916 (3)	0.3399 (2)	0.3618 (3)	0.0383 (7)
C32	0.8858 (3)	0.3324 (2)	0.4613 (3)	0.0454 (8)
C33	0.9091 (3)	0.2679 (2)	0.4900 (2)	0.0450 (8)
C34	0.9303 (2)	0.2337 (2)	0.4093 (2)	0.0348 (6)

Table 2. Selected geometric parameters (Å, °)

Siemens P4 diffractometer	θ _{max} = 27.50°
θ/2θ scans	<i>h</i> = -1 → 14
Absorption correction: none	<i>k</i> = -1 → 26
	<i>l</i> = -18 → 17

Sn—O2	2.111 (2)	P2—O2	1.502 (2)
Sn—O1	2.127 (2)	P1—C1	1.789 (3)
Sn—C14	2.3710 (11)	P1—C7	1.805 (3)
Sn—C13	2.3779 (10)	P1—C25	1.784 (3)

Sn—C12	2.3818 (10)	P2—C13	1.790 (3)
Sn—C11	2.3894 (9)	P2—C19	1.794 (3)
P1—O1	1.505 (2)	P2—C30	1.773 (3)
O2—Sn—O1	85.31 (8)	O1—P1—C25	112.97 (13)
O2—Sn—C14	86.22 (6)	O1—P1—C1	111.30 (14)
O1—Sn—C14	86.09 (6)	C25—P1—C1	106.58 (14)
O2—Sn—C13	84.77 (6)	O1—P1—C7	108.06 (14)
O1—Sn—C13	85.88 (6)	C25—P1—C7	106.83 (14)
C14—Sn—C13	168.38 (3)	C1—P1—C7	111.03 (14)
O2—Sn—C12	90.94 (6)	O2—P2—C30	113.54 (13)
O1—Sn—C12	176.15 (6)	O2—P2—C13	108.46 (13)
C14—Sn—C12	94.55 (4)	C30—P2—C13	108.09 (14)
C13—Sn—C12	92.91 (4)	O2—P2—C19	112.87 (13)
O2—Sn—C11	174.65 (6)	C30—P2—C19	106.37 (13)
O1—Sn—C11	89.39 (6)	C13—P2—C19	107.24 (14)
C14—Sn—C11	92.71 (4)	P1—O1—Sn	161.52 (14)
C13—Sn—C11	95.58 (4)	P2—O2—Sn	158.88 (14)
C12—Sn—C11	94.37 (4)		

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Chlorobis[2-(diphenylphosphino)-phenolato-*O,P*]oxorhenium(V)

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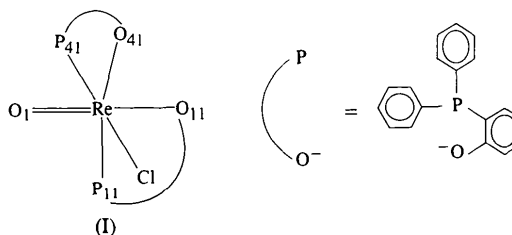
(Received 16 February 1996; accepted 25 March 1996)

Abstract

The title compound, [ReClO(C₁₈H₁₄OP)₂], contains severely distorted octahedra with a *cis,cis,cis* configuration. One of the phenolate O atoms is *trans* to the Re=O bond, whereas the two P atoms occupy *cis* sites. Departure from octahedral geometry can be interpreted in terms of the steric hindrance between the phosphine groups, the small bite of the P—O chelating agent and the tendency of the Re=O bond to repel the adjacent bonds. Bond lengths are Re=O 1.686 (4), Re—Cl 2.394 (2), Re—P 2.443 (2) and 2.451 (2), and Re—O(phenolate) 2.003 (4) (*trans* to Re=O) and 1.987 (4) Å (*trans* to P).

Comment

Chlorobis[2-(diphenylphosphino)phenolato-*O,P*]oxorhenium(V), (I), was prepared as part of our ongoing research into rhenium complexes with various P—O chelating agents of potential interest in radiopharmacy. While this work was in progress, the same complex was prepared *via* a different route by Luo, Setyawati, Rettig & Orvig (1995). The present crystallographic study confirms the geometry proposed by those authors from NMR data.



The crystal structure of (I) contains highly distorted *cis,cis,cis*-octahedral molecules (Fig. 1). The metal is a chiral centre and all molecules in the crystal studied have an absolute *C* configuration. The bulk sample is racemic, however, as evidenced from the zero rotatory power measured in CH₂Cl₂.

Departure from idealized octahedral geometry (Table 2) can be rationalized from the three factors discussed

The title structure was solved by direct methods and refined by full-matrix least-squares techniques. All H atoms were located from difference maps and refined isotropically.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990a). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL/PC (Sheldrick, 1990b). Software used to prepare material for publication: SHELXL93. Geometric calculations: PARST (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1088). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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